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Phosphorus capture recycling and utilization for sustainable agriculture using Al/organic composite water treatment residuals

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Phosphorus capture, recycling and utilization for sustainable agriculture and a clean environment using Al/Organic Composite water treatment residuals (Al/O-WTR)

Summary

Objectives: 1) develop a thorough understanding of the sorption mechanisms of Pi and Po onto the Al/O-WTR; 2) determine the breakthrough range of the composite Al/O-WTR during P capturing from agro-wastewaters; and 3) critically evaluate the performance of the composite Al/O-WTR as a fertilizer using selected plants grown in lysimeters and test-field studies. Instead of lysimeters we used pots (Israel) and one-liter cone-tainers (USA). We conducted one field study but in spite of major pretreatments the soils still exhibited high enough P from previous experiments so no differences between control and P additions were noticeable. Due to time constrains the field study was discontinued.
Background: Phosphorous, a non-renewable resource, has been applied extensively in fields to increase crop yield, yet consequently has increased the potential of waterway eutrophication. Our proposal impetus is the need to develop an innovative method of P capturing, recycling and reuse that will sustain agricultural productivity while concurrently reducing the level of P discharge from and to agricultural settings.
Major Conclusions & Achievements: An innovative approach was developed for P removal from soil leachate, dairy wastewater (Israel), and swine effluents (USA) using Al-based water treatment residuals (Al-WTR) to create an organic-Al-WTR composite (Al/O-WTR), potentially capable of serving as a P fertilizer source. The Al-WTR removed 95% inorganic-P, 80% to 99.9% organic P, and over 60% dissolved organic carbon from the agro-industrial waste streams. Organic C accumulation on particles surfaces possibly enhanced weak P bonding and facilitated P desorption. Analysis by scanning electron microscope (SEM-EDS), indicated that P was sparsely sorbed on both calcic and Al (hydr)oxide surfaces. Sorption of P onto WW-Al/O-WTR was reversible due to weak Ca-P and Al-P bonds induced by the slight alkaline nature and in the presence of organic moieties. Synchrotron-based microfocused X-ray fluorescence (micro-XRF) spectrometry, bulk P *K*-edge X-ray absorption near edge structure spectroscopy (XANES), and P *K*-edge micro-XANES spectroscopy indicated that adsorption was the primary P retention mechanism in the Al-WTR materials. However, distinct apatite- or octocalcium phosphatelike P grains were also observed. Synchrotron micro-XRF mapping further suggested that exposure of the aggregate exteriors to wastewater caused P to diffuse into the porous Al-WTR aggregates. Organic P species were not explicitly identified via P *K*-edge XANES despite high organic matter content, suggesting that organic P may have been predominantly associated with mineral surfaces. In screen houses experiments (Israel) we showed that the highest additions of Al/O-WTR (5 and 7 g kg^{-1}) produced the highest lettuce (*Lactuca sativa* L. var. *longifolial*) yield. Lettuce yield and P concentration were similar across treatments, indicating that Al/O-WTR can provide sufficient P to perform similarly to common fertilizers. A greenhouse study (USA) was utilized to compare increasing rates of swine wastewater derived Al/O-WTR and inorganic P fertilizer (both applied at 33.6, 67.3, and 134.5 kg P_2O_5 ha^{-1}) to supply plant-available P to spring wheat (*Triticum aestivum* L.) in either sandy loam or sandy clay loam soil. Spring wheat straw and grain P uptake were comparable across all treatments in the sandy loam, while Al/O-WTR application to the sandy clay loam reduced straw and grain P uptake. The Al/O-WTR did not affect soil organic P concentrations, but did increase phosphatase activity in both soils; this suggests that Al/O-WTR application stimulated microorganisms and enhance the extent to which microbial communities can mineralize Al/O-WTR-bound organic P.
Implications: Overall, results suggest that creating a new P fertilizer from Al-WTR and agro-industrial waste sources may be a feasible alternative to mining inorganic P fertilizer sources, while protecting the environment from unnecessary waste disposal.

Summary Sheet

Publication Summary

PubType	IS only	Joint	US only
Reviewed	0	4	0

Training Summary

Trainee Type	Last Name	First Name	Institution	Country
Postdoctoral Fellow	Zohar	Iris	MIGAL - Galilee Research Institute	Israel
M.Sc. Student	Shechter	Shai	Migal Galilee Technology Center	Israel
M.Sc. Student	Banet	Travis	CSU	USA
Postdoctoral Fellow	Zohar	Iris	MIGAL	Israel

Contribution of the collaboration

The PI has been involved in many research projects over the years including NSF funded Niwot Ridge LTER, EU funded FP-5, FP-6, FP-7, Horizon 2020, COST 869, and the German BMBF funding of the GLOWA project. In most of these projects the collaboration was limited to meetings and verbal consultation with limited genuine mutual contribution. This is NOT the case in this study. The Israeli PI travel twice to Colorado State University - CSU (second trip was funded by MIGAL) and we worked together on reports, manuscripts, and generated new ideas that culminated to another newly funded BARD project to commence December 2019. During the first trip to CSU we analyzed the results and concluded that the USA team should work on swine wastewaters rather than dairy effluents in order to enlarge the scope of the study beyond what we originally proposed to the BARD. During this visit the Israeli PI also travelled to California and worked closely with our associate analyzing the results received from the synchrotron. Since here in Israel we do not have a synchrotron the collaboration with Dr. Mike Massey of California State University was essential to get in-depth understanding of the sorption mechanisms of P onto Al/O-WTR surfaces. Last year, the CO-PI travelled to Israel, visited our lab in MIGAL and for several long days we were engaged in discussions of the results and analyzing paths forward. Perhaps, the most convincing testimony of our very close collaboration and mutual contributions are the already four published papers in leading journals and three more were written, one in review and two will be submitted by November 2019 to STOTEN.

Phosphorus capture, recycling and utilization for sustainable agriculture and a clean environment using Al/Organic Composite water treatment residuals (Al/O-WTR)

Achievements - Significance of main scientific achievements and agriculture impacts

We showed that modified Aluminum water treatment residual (Al-WTR), into organic composite termed Al/O-WTR, had improved P desorption over Al-WTR reacted with purely inorganic P. Weaker P sorption was likely induced by the presence of organic compounds originating from treating polluted waste streams such as swine and dairy wastewaters (WW) with Al-WTR. The original Al-WTR exhibited an excellent capacity of removing SRP (95%), non-SRP (80% - 99.9%) and to a lesser extent, DOC (60%) from polluted waste streams. Opposite trends were observed for desorption, with solids tending to retain SRP and release OM. It appears that as the P load increased, surface accumulation was promoted. Otherwise, the chemical composition of the Al-WTR and Al/O-WTRs was very similar and indicated the presence of organic C, Al and Fe hydr(oxides), Si, clays, and Ca precipitates. P binding mechanisms likely involved both sorption onto sites of various strength in the (organic) alum composites, and precipitation as Ca-P or Al-P solids, on surfaces as well as in intra-aggregate pores (Zohar et al., 2017).

Further examination of P sorption onto the Al-WTR and the WW-Al/O-WTR in sorption experiments and with scanning electron microscopy (SEM-EDS) suggested multifaceted P sorption behavior, which were also identified by P K-edge XANES (Massey et al., 2018). The sorption isotherms implied change in sorption type above P addition of 100 to 500 mg L^{-1}, whereas three-element overlay maps were useful in elucidating P associations and distribution. Phosphorus was predominately associated with amorphous Al (hydr)oxides, whereas areas dominated by Ca were also important for P sorption. Slight alkaline pH and the large areas of P associated with $CaCO_3$ potentially decreased the Al surface sorption capacity. Organic-rich dairy wastewaters were a good source of P, while concurrently the organic substances affected P sorption associations, distribution, and solubility. Phosphorus sorption with Al and Ca in the WW-Al/O-WTR was of more clustered nature, including in a ternary phase, yet P became more soluble. Thus, after the Al-WTR efficient recapturing of P from the dairy wastewater, P sorption characteristics were affected, making the final product, the WW-Al/O-WTR, a good source for P and supporting our initial hypothesis (Zohar et al., 2018; Massey et al., 2018).

Phosphorous sorption on the Al-WTR occurred on both Al and Ca surfaces, with Al surfaces being the dominant adsorbent on reaction of Al-WTR with dairy wastewater. Phosphorus recycling using Al-WTR formed in high-Ca, alkaline surface water is advantageous, as P is sorbed efficiently by the various adsorbents, promising high P removal from water. The alkaline conditions, in turn, support relatively weak bonding of P to calcite surfaces, possibly and eventually promoting greater P availability when the Al-WTR are applied as a fertilizer alternative. Previous work evaluated Al-WTR as a soil "alternative" or soil conditioner, although the P sorption step evaluated in this study seems crucial for the use of Al-WTR as a P source for crops. Using waste products like Al-WTR for P recycling from organic matter-containing liquid waste streams may be more challenging than synthetic materials, due to their heterogeneous composition. However, the presence of multiple physically and chemically distinct P domains and P sorption mechanisms in the Al-WTR (ranging from P adsorbed on Ca-rich surfaces, to P adsorbed on amorphous Al oxides, to distinct grains of apatite or octocalcium phosphate, to P sorbed on the interior of aggregates) may actually contribute to a material capable of supplying a range of P concentrations usable as a P fertilizer, across a single growing season or even across multiple years (Massey et al., 2018).

Following the laboratory analyses and results summarized above we conducted a test study of making P fertilizer from dairy wastewaters with Al-WTR. The results strongly support the hypothesis that Al-WTR can capture P from organic matter-rich, high P concentration dairy wastewater and release this essential nutrient in P-poor soil to support lettuce growth (*Lactuca sativa* L. var. *longifolial*) with comparable efficacy to commercialized fertilizer. The addition of Al/O-WTR to slightly alkaline soils provided a P source rather than a P sink, and did not cause Al toxicity. Therefore, conversion of Al-WTR to Al/O-WTR can transform water treatment residuals into a P-rich resource, which may offset somewhat the mining of this non-renewable resource (Litaor et al., 2019).

Concurrently to the screen house study we performed an additional study of P fractionation of Al and Fe-based water treatment residuals using sequential extraction procedures. Most of the P in Al-based WTRs was associated with Al (hydr)oxides and authigenic and detritus Ca, including $CaCO_3$ surfaces. In the Fe-based WTRs, Fe (hydr)oxides accounted for most P sorption, while Ca-bound P was relatively a small pool. A shift in P pools proportions in Al- and Fe-based WTRs was recorded following mixing with dairy WW, from strongly bound and occluded P pools to relatively moderately labile fractions. The WW-Al/O-WTR had a higher P load compared to the WW-Fe/O-WTR, yet higher P lability in the latter vs. the former (30% and 5% labile P pool proportion, respectively) increases the potential of WW-Fe/O-WTR to become an alternative P fertilizer. Inorganic P displays better affinity to the trivalent (hydr)oxides than Po (Zohar et al., *in review*).

After the initial results with dairy wastewaters we decided that the complementary study in the USA will be conducted using swine effluents. The results supported the hypothesis that mixing Al-WTR with swine wastewater would sorb as well as readily desorb organic P over time. Our data conclusively illustrated that Al-WTR has the ability to quickly and efficiently remove organic P from agricultural waste streams such as swine wastewater, and that the resulting Al/O-WTR has a relatively high propensity to release organically sorbed P. In combination, these results show promise for large-scale Al/O-WTR generation, and its potential for supplying P as a soil amendment (Travis et al., to be submitted November, 2019 to STOTEN).

Green house study in Colorado suggested that the capacity for Al/O-WTR to supply plant-available P is dependent on soil texture and related properties. This research serves as evidence to suggest that Al/O-WTR may be a comparably effective source of plant-available P in low clay content soils when compared to inorganic P fertilizers. Thus, the hypothesis that Al/O-WTR can comparably supply plant-available P to soils for plant uptake was accepted in the sandy loam soil but rejected in the sandy clay loam soil. Repurposing Al-WTR and swine wastewater to generate Al/O-WTR as a plant-available P supply has limitations dependent upon soil textural properties. Advancing technologies and management strategies to promote zero waste are essential to maintaining long term food security and agroecosystem sustainability (Travis et al., to be submitted to STOTEN).

Changes to Original Research Plan

Task 1, Al/O-WTR Composites - Formation and Evaluation – *Done*

Task 2, Sequential Extraction experiment – *Done*

Task 3, Spectroscopically Evaluate P Sorption Mechanism in Al/O-WTR – *Done*

Task 4, Lysimeter Experiment – *Modified. We opted to use generic pots (Israel) and cone-tainers (USA) instead of the lysimeters because of ease of operation and cost associated with the construction of lysimeter 's station.*

Task 5, Test Plot Al/O-WTR P addition Experiment – *We conducted one experiment in a test plot located in the research farm in Upper Galilee, Israel. P extraction showed that the soil exhibited over 30 mg kg^{-1} Olsen-P. To reduce the available P we sown corn without P addition and after 4 months the Olsen P in the plot decrease to 24 mg kg^{-1} Olsen P. Next we ploughed the soil and the average Olsen P was further reduced to 16 mg kg^{-1}. This is approximately half the recommended bio-available P for lettuce according to the Israeli field extension recommendations. We launched a full scale multifactor experiment but apparently the amount of P in these soils was still sufficient so no statistical differences were observed between the control plots and the various Al/O-WTR addition plots and the commercialized fertilizer plots. Time constrains, high cost and luck of other plots availability in the research farm dictated the abandonment of additional experiment.*

Publications for Project IS-4870-15 R

Status	Type	Authors	Title	Journal	Vol:pg Year	Coun
Published	Reviewed	*1. Zohar, I. J. Ippolito, M. S. Massey, M.I. Litaor*	Innovative approach for Recycling Phosphorous from Agro-Wastewaters Using Water Treatment Residuals (WTR)	***Chemoshpere***	168 : 234-243 2017	Joint
Published	Reviewed	*2. Zohar, I., M. S. Massey, J.A. Ippolito, and M. I. Litaor*	Phosphorus Sorption Characteristics in Aluminum-Based Water Treatment Residuals Reacted with Dairy Wastewater, Part I: Isotherms, XRD, and SEM-EDS Analysis	***Journal Environemental Quality***	: 2018	Joint
Published	Reviewed	*3. Massey, M.S., I. Zohar, J.A. Ippolito, and M.I. Litaor*	Phosphorus sorption to aluminum-based water treatment residuals reacted with dairy wastewa¬ter, Part II: X-ray adsorption spectroscopy	***Journal Environemental Quality***	: 2018	Joint
Published	Reviewed	*4. Litaor, M.I., S. Schechter, I. Zohar, M.S. Massey, J. A. Ippolito*	Making Phosphorus Fertilizer from Dairy Wastewater with Al Water Treatment Residuals	***Soil Science Society of America Journal***	: 2019	Joint

Appendix

Published papers

1. Zohar, I. J. Ippolito, M. S. Massey, M.I. Litaor. 2017. Innovative approach for Recycling Phosphorous from Agro-Wastewaters Using Water Treatment Residuals (WTR). Chemoshpere, 168: 234-243.
2. Zohar, I., M. S. Massey, J.A. Ippolito, and M. I. Litaor. 2018. Phosphorus Sorption Characteristics in Aluminum-Based Water Treatment Residuals Reacted with Dairy Wastewater, Part I: Isotherms, XRD, and SEM-EDS Analysis Journal Environemental Quality. doi:10.2134/jeq2017.10.0405
3. Massey, M.S., I. Zohar, J.A. Ippolito, and M.I. Litaor. 2018. Phosphorus sorption to aluminum-based water treatment residuals reacted with dairy wastewater, Part II: X-ray adsorption spectroscopy. Journal Environmental. Quality. doi:10.2134/ jeq2017.10.0407 .
4. Litaor, M.I., S. Schechter, I. Zohar, M.S. Massey, J. A. Ippolito. 2019. Making Phosphorus Fertilizer from Dairy Wastewater with Al Water Treatment Residuals. Soil Science Society of America Journal. doi:10.2136/sssaj2018.07.0278.

Unpublished Papers (*In review or advanced preparations*)

1. Banet, T., I. Zohar[c], M.I. Litaor[c], M. Massey, and J. A. Ippolito (*in preparation*). Phosphorus Removal from Swine Wastewater Using Aluminum-Based Water Treatment Residuals. Science of the Total Environment (to be submitted).
2. Zohar, I., J. Ippolito, M. Iggy Litaor (*in review*). Phosphorus fractionation of aluminum- and iron-based water treatment residuals (WTRs) using sequential extraction procedures. JEQ.
3. Banet, T., M. Massey, I. Zohar, M.I. Litaor, and J. Ippolito (*in preparation*). Assessing Modified Aluminum-Based Water Treatment Residuals as a Plant-Available Phosphorus Source. Science of the Total Environment (to be submitted).

Conferences

Banet, T., J. Ippolito, M. Massey, I. Zohar, and I. Litaor. 2019. Repurposing municipal and agricultural waste products to benefit water quality, ecosystems, and agricultural sustainability. American Society of Agronomy Meetings. November 10-13. San Antonio, TX.

Banet, T., J. Ippolito, M. Massey, I. Zohar, and I. Lataor. 2019. Repurposing municipal and agricultural waste products to benefit water quality, ecosystems, and agricultural sustainability. Demo Days. Colorado State University. April 23.

Banet, T., J. Ippolito, M. Massey, I. Zohar, and I. Litaor. 2018. Aluminum water treatment residuals retain organic phosphorus that may be used as a potential plant-available source. American Society of Agronomy Meetings. November 4-7. Baltimore, MD.

Banet, T., J. Ippolito, M. Massey, I. Zohar, and I Litaor. 2018. Aluminum water treatment residuals can capture organic phosphorus to be used as a potential plant-available source. Great Plains Soil Fertility Conference. Denver, CO. March 6-7.

Theses

Banet, T. 2019. Repurposing agriculture and municipal wastes to supply soil with plant-available phosphorous.

Schechter, S. 2017. Using aluminum water treatment residual (Al-WTR) for capturing phosphorus from dairy wastewater and reuse it as a fertilizer: case study with lettuce.